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Sol-gel synthesized dielectric films as a diffusion barrier to rear side contact metal

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Abstract

It is essential to mitigate the costs of cell production in order to achieve an increasing share of the industrial manufacture of advanced and more efficient solar cells. This work aims to contribute to the efficiency enhancement and cost reduction of rear contact cells, such as passivated emitter rear contact (PERC) cells. In order to realize these goals, various dielectric materials are proposed that mainly function as a diffusion barrier to the rear contact metal, i.e. aluminum as well as impurities. Dielectric materials that are formulated as chemical solutions are coated on single-side-polished, monocrystalline silicon. Their barrier function is tested with three different screen-printable aluminum pastes. Among various materials, five inks showed an absolute barrier behavior against different aluminum pastes. Furthermore, the compatibility of these materials with the existing passivation layer, ALD-AlOx, (AlOx film deposited by atomic layer deposition) is imaged by photoluminescence spectroscopy. The minimum film thickness that is necessary for preventing aluminum penetration is determined by scanning electron microscopy (SEM) and ellipsometry. This is found to be 450 nm for the cured dielectric material that showed the best overall results.

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Keywords: sol-gel synthesis, dielectric film, diffusion barrier, rear side metallization

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1. Motivation

The proposed dielectric materials are synthesized by the low-cost sol-gel method. Theoretically, it is possible to formulate sol-gel solutions in a way that inkjet printable, spray coatable inks as well as screen printable pastes can be obtained. In order to focus on the proposed material's test results, the functional formulation phase in the beginning has been omitted. The standard PERC cell concept is taken as a reference application, where the rear side comprises a thin ALD-AlO_x layer, a SiN_x layer on top of that and screen-printed aluminum paste as rear side contact metal [1]. Considering the complex and costly application of SiN_x, and the efficiency decreasing contact opening steps [2], [3], printable/coatable dielectric materials would be very advantageous for the industrial feasibility of PERC cells.

2. Experiment

The inks were deposited by the spin-coating method that is coupled to a drying step performed at 400 °C for 10 min on a hotplate, whereas single-side-polished, monocrystalline silicon was used as a test substrate. Various film thicknesses of dielectric layers (DL-1 to DL-5) were prepared with each ink in order to find the minimum film thickness that is required to prevent the aluminum spiking. The dielectric layers above the material-specific critical film thickness were reached by multiple application of coating-drying cycles. For a more accurate interpretation of the materials, three different commercially available screen printable Al-metallization pastes (MP1 – MP3) were applied that are convenient for local back surface field formation. Chosen aluminum pastes were doctor-bladed onto spin coated dielectric layers in order to achieve around 40 µm thick wet films that were then dried at 150 °C for 2 min. These prepared dielectric layer/aluminum paste stacks were fired at temperatures of 850 °C and 900 °C. Figure 1 shows a typical firing temperature profile for the industrial rear side contact formation [4], while Figure 2 shows the temperature profile that is applied for testing the coatable barrier materials with the set temperature of 900 °C. The contact firing profile that we applied provides substantially more severe conditions with respect to the standard. By applying such high-limit conditions it is possible to determine the limitations of the dielectric material to be probed.

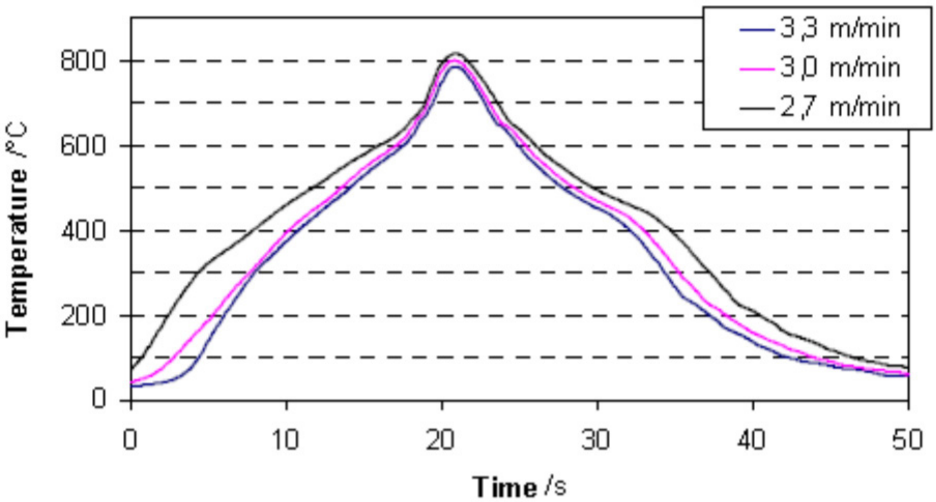

Fig. 1. Example of a temperature profile for the rear side metallization of a PERC cell [4].

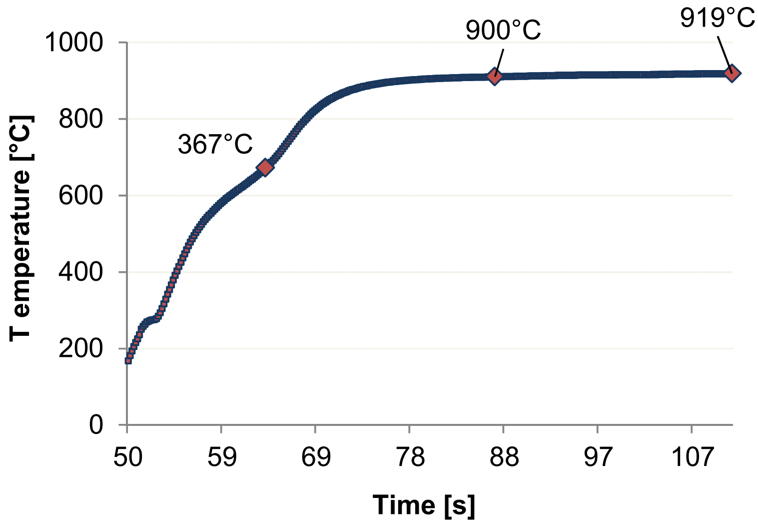

Fig. 2. Temperature profile that is applied for the tests with the contact firing process at 900 °C for 1min. The one-minute time period started at 367 °C and ended at 919 °C in reality.

Samples were observed by SEM imaging after the metallization process. The optical evaluation of the surfaces was carried out by optical microscopy and white light interferometry after the stacks of dielectric layers and aluminum pastes were etched off by treating the samples first with 40% H_3PO_4 and then with 2% HF. The possible diffusion of the aluminum into the silicon sample was observed by electrochemical capacitance voltage (ECV) measurement. The obtained carrier depth profile was confirmed by the application of secondary ion mass spectrometry (SIMS) for some samples.

For a possible application of these dielectric layers on the rear side of the PERC cells, their chemical and thermal compatibility with a passivating ALD-AlO_x layer was observed by photoluminescence imaging. The dielectric materials were deposited onto ALD-AlO_x by multiple steps of coating and drying as mentioned before. Half of the samples were metallized by screen-printing the aluminum paste. Photoluminescence imaging was carried out before and after metallization of the samples.

3. Results

The outcome of these barrier tests indicate that, among various inks, five specific prototypes show promising results. A critical film thickness of 100 - 165 nm, which is delivered by single-step coating, is not adequate to prevent the aluminum spiking. This suggested us to test multiple layer samples. On the surface of the single-layer samples, one can observe an Al-Si eutectic layer formation. This formation is weakened by the double layer and instead appears as pyramidal holes on the substrate surface that is caused by local spiking. This phenomenon is depicted by Wijekoon et al. (2013) among others [5]. The level of the surface damage is observed by optical microscopy and white light interferometry. The metallized areas were mapped and the acquired images were evaluated for the percentage amount of black pixels that correspond to the concentration of the inverted pyramids. As a result of this quantification the surface damage of the samples was classified by digits 0 to 4 (Table 1).

Table 1. Optical evaluation of the surface defects after all the layers were etched off.

Process	**Coating Steps**	**Damage Concentration**														
		DL-1			**DL-2**			**DL-3**			**DL-4**			**DL-5**		
		MP1	MP2	MP3	MP1	MP2	MP3	MP1	MP2	MP3	MP1	MP2	MP3	MP1	MP2	MP3
850 °C 1min	Double	3	3	4	3	2	4	4	3	2	2	1	3	1	2	4
	Triple	1	2	1	0	0	1	4	2	1	0	1	1	0	3	1
	Quadruple	0	0	1	-	-	-	-	-	-	-	-	-	0	0	1
900 °C 1min	Triple	2	4	4	0	0	4	4	4	2	2	1	3	1	4	4
	Quadruple	1	4	4	0	0	4	4	4	0	0	0	3	1	4	4
0: no damage, **1:** up to 0.1%, **2:** 0.1 to 1% **3:** 1 to 10%, **4:** over 10% **DL:** Dielectric layer **MP:** Metallization paste																

As shown by the table, dielectric materials have different durabilities against different metallization pastes. DL-1, DL-2 and their related formulations provide a barrier against MP1 and MP2, whereas DL-3 can only barrier MP3. These might be caused by different glass frit contents of the metal paste, which is not specified by the supplier. The film thickness of the samples that are encoded with green in Table 1 were determined by spectroscopic ellipsometry after the metallization process and are listed in Table 2. This table shows practically the minimum film thicknesses of each dielectric material that blocked a metallization paste.

Table 2. Thickness of each dielectric layer that is proved to be a barrier for an applied metal paste. The film thicknesses were determined after the metallization process.

Process temperature	Film thicknesses after the metallization process				
	DL-1	DL-2	DL-3	DL-4	DL-5*
850 °C, 1min	341 nm	286 nm	-	274 nm	462 nm
900 °C, 1min	-	284 nm	337 nm	338 nm	-

*A quadruple-coated dielectric layer was taken as an absolute barrier at 850 °C

The most striking result is obtained with the triple layer of the DL-2. DL-2 film that works as an adequate barrier for both process temperatures, is verified as 450 nm after drying at 400 °C and 284 nm after at 900 °C. The diffusion profile is screened by ECV measurement as a proof. Even this method has limitations by low-doped samples, a difference between a slightly doped region and a shielded region could be distinguished. The standard pattern of all the non-doped and very low-doped sample's profiles are starting at 0.5 - 1 µm deeper from the surface. This is correlated with the width of the depletion region. As the equation (Eq. 1) underlying the electrochemical characterization method describes, the decrease of doping atoms widens the depletion region. This reflects on the measurements as a deepened profile [6].

$$W = \sqrt{\frac{2\varepsilon_{Si}\varepsilon_0\varphi_S}{qN_A}} \qquad (1)$$

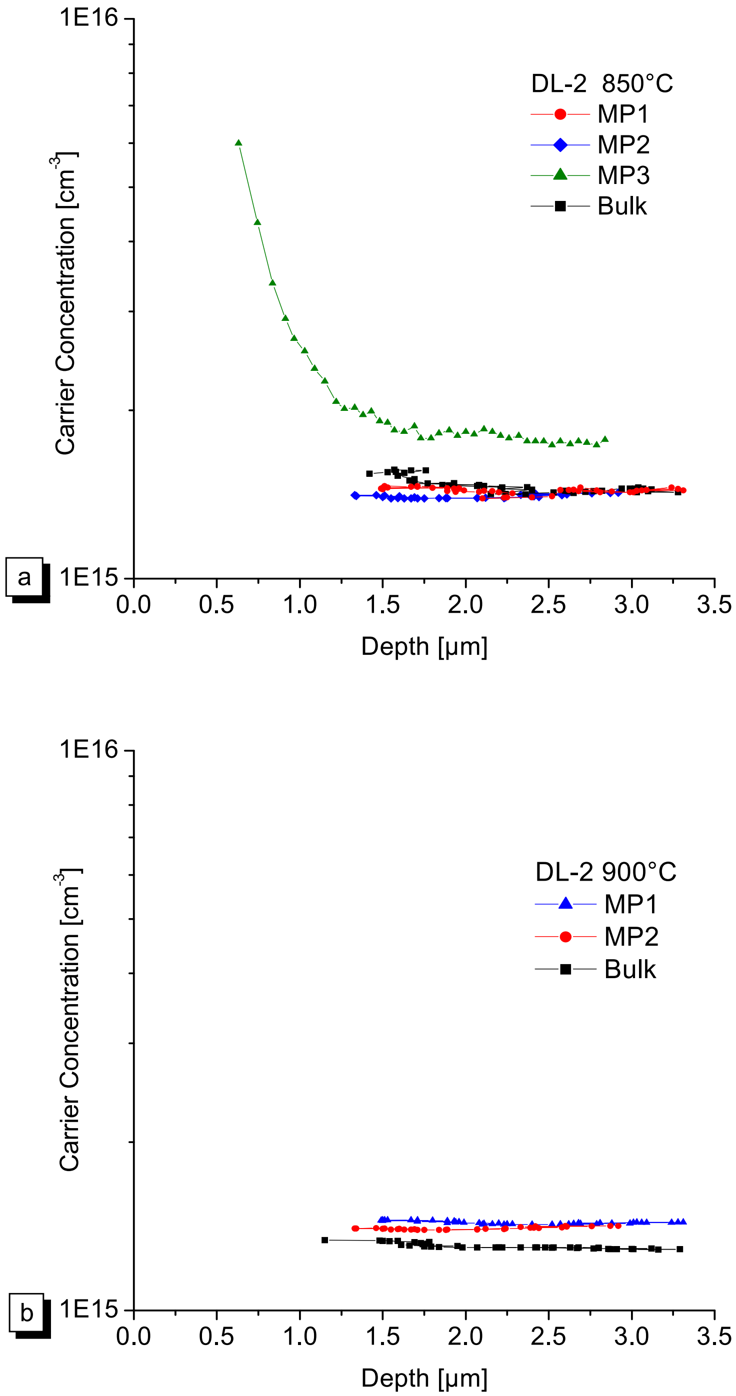

Fig.3. ECV profile of samples that were coated with approx. 280 nm thick DL-2, metallized with three commercial LBSF pastes MP1, MP2 and MP3, and fired at 850 °C (a) and 900 °C (b). The layers were etched off by 40% H_3PO_4 and 2% HF prior to ECV measurement. The bulk is the region on samples that was coated with dielectric material but not metallized.

The depth profiles of the DL-2 samples metallized at 850 °C and 900 °C are shown in Figure 3. The region on the same sample that is not metallized, i.e. bulk silicon, is also depicted as a comparison.

For the samples DL-3 and DL-4, the aluminum penetration is detected both by SIMS and ECV measurements. Figures 4 and 5 show respectively the SIMS profile and the ECV profile of 338 nm thick DL-4 film, processed at 900 °C. The elevated surface concentration around 0.2 µm depth can be assigned to surface residues after etching off the layers, since bulk profile (the not metallized dielectric region) has the same effect. The regression line of the bulk silicon profile can be considered as a background aluminum concentration, which is around $1.8*10^{14}$ cm^{-3}. The profile of MP3 can be regarded as a reference for an evidently doped area. However, a certain deviation of this profile due to the high amount of surface damage has to be taken into account. Even if both diffusion profiles are not superimposed due to the different atom types (aluminum concentration for SIMS, and combined aluminum and boron concentration for ECV), the low-doped region and the not doped region could be distinguished with both methods.

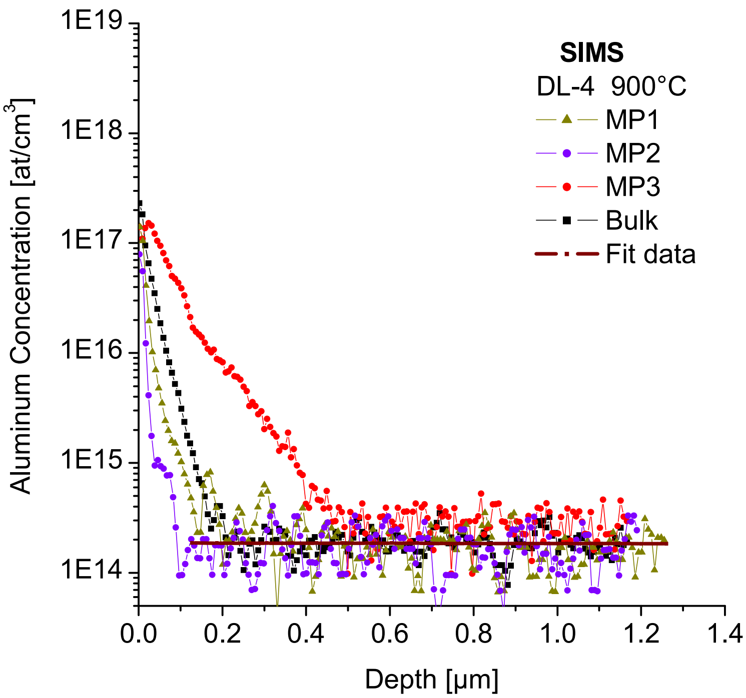

Fig.4. SIMS profile of the sample coated with 338 nm DL-4 that was metallized at 900 °C for 1 min. MP1, MP2 and MP3 are the metallized regions, and the bulk region is coated with DL-4 but not metallized.

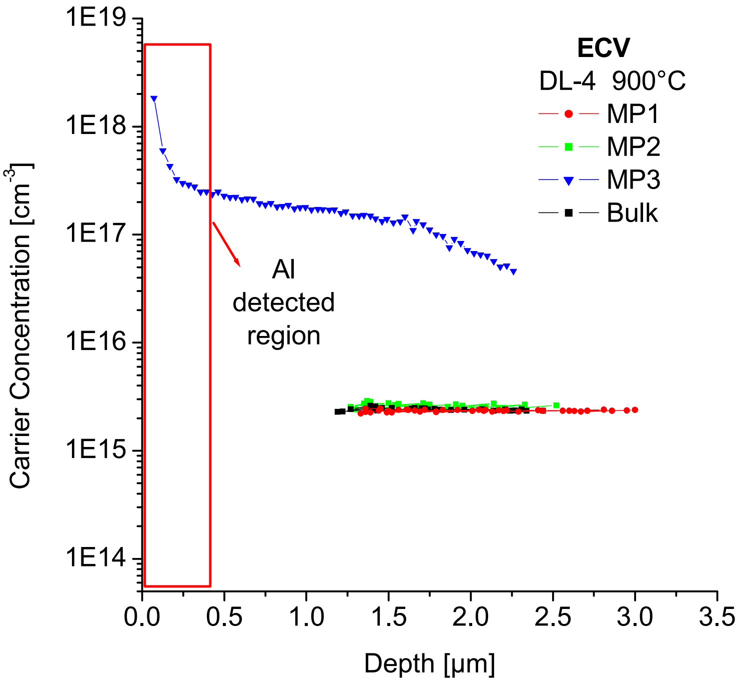

Fig.5. ECV profile of the same sample. MP1, MP2 and MP3 are the metallized regions, and the bulk region is coated with DL-4 but not metallized. The dashed line shows the Al-detected region according to the SIMS profile.

The diffusion profile with DL-3 coated sample indicates that 269 nm film is not adequate for metallization at 850 °C. In order to build a barrier with DL-3, a 450 nm film thickness is required. However, this material would be eligible only if MP3 is the applied metallization paste.

DL-1 and DL-5 showed similar results. The required film to block MP1 and MP2 diffusion at 850 °C is 340 nm for DL-1 and 460 nm for DL-5. In order to achieve these film thicknesses, they both require a four-step coating process. Figure 6 shows the diffusion profiles of samples that were coated with DL-1 and DL-5 and metallized at 850 °C. For a better comparison, the profile of the aluminum-penetrated region (MP3) and the non-metallized region (bulk) are also shown in Figure 6.

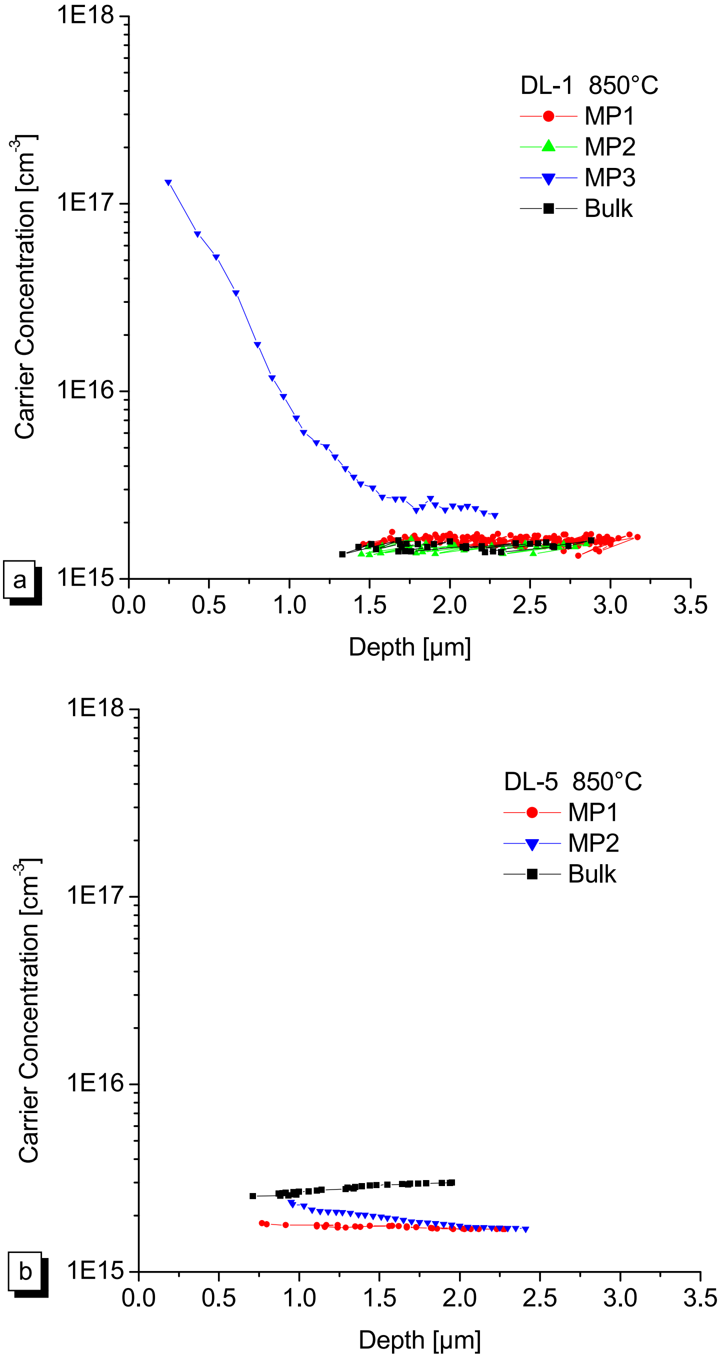

Fig. 6. ECV profile of the samples coated with 340 nm DL-1 (a) and 460 nm DL-5 (b) that were both metallized at 850 °C.

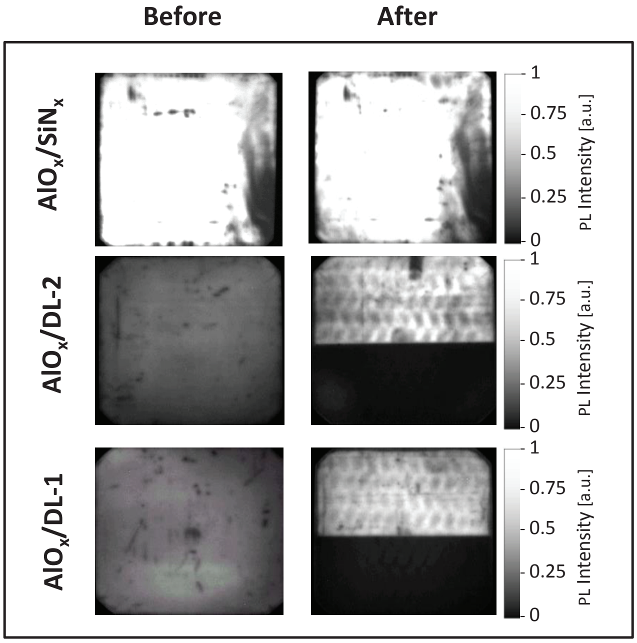

Fig.7. Passivation quality measured by photoluminescence imaging. Dielectric layers were deposited onto ALD-AlO_x film by multiple spin coating steps. The lower parts of the wafer were metallized. Photoluminescence imaging was performed before and after metallization.

In addition to the diffusion tests, the compatibility of the dielectric film with the ALD-AlO_x passivation layer was tested by photoluminescence imaging. The wafers (CZ) used in this procedure comprised a typically acid-based wet chemically polished rear surface as well as textured front sides. The films were deposited by spin coating onto an ALD-AlO_x layer and dried at 400 °C for 10 min multiple times on a hotplate. Subsequently, half of the wafers (lower part according to Figure 7) were metallized. Before and after the metallization step, PL measurement was carried out. A reference wafer that has the stack of ALD-AlOx/SiNx was processed and measured as a comparison. As shown in Figure 7, two of the proposed dielectric films preserved the passivation provided by the ALD-AlO_x film. Although the passivation is not as good as the reference sample with the AlO_x/SiN_x stack, considering the multiple coating and its associated multiple drying steps, it can be concluded that the tested dielectric barriers have improvement potential.

Due to the inhomogeneous coverage of post-polished textured surfaces as a result of coating method, aluminum spiking was observed on the metallized part of the samples. According to SEM image, film thickness varies from 180 nm to 750 nm between top and valley, respectively (Fig. 8). In future attempts, it is suggested that the homogeneity could be improved by formulation of spray coating or screen printable inks.

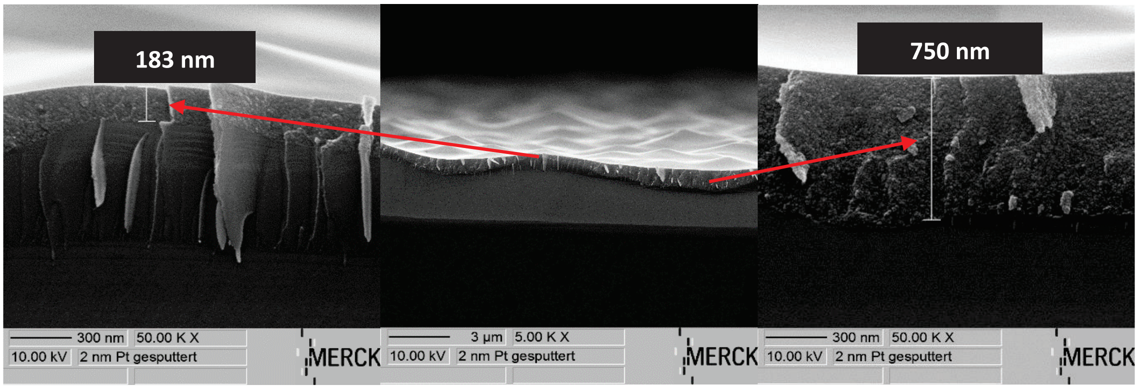

Fig. 8. An example of an inhomogeneous film on texture that is deposited by spin coating.

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